# Isotopic Composition of Runoff in Large Catchments in Southern Africa

**A. S. Talma[1] and S. A. Lorentz[2]**

[1]Division of Water, Environment and Forestry Technology, CSIR, P.O. Box 395, Pretoria, 0001.

[2]School of Bioresources, Engineering and Environmental Hydrology, University of KwaZulu-Natal, P.O. Box X01, Scottsville, 3209.

## Abstract

Stable isotopes (oxygen-18 and deuterium) were employed as tracers to follow water sources and evaporation processes in rivers from 11 large catchments in southern Africa in 1968 to 1973. A recent sampling program was initiated in 2003 as part of an worldwide project to employ isotopes to study large river basins. The present sampling network consists of a number of stations along the Zambezi, Orange and Tugela Rivers and provides a comparison of the changes over 30 years.

The $^{18}O$ data of undisturbed rivers show a saw-tooth pattern negatively correlated with flow. Changing land-use, in particular the construction of large reservoirs during the last three decades, have caused changes of the $^{18}O$ time series from the 1970's to the present time. Large dams in which water is stored for months to years tend to smooth out both flow and isotope variations. Isotope characteristics of base flow are probably typical of water stored along river embankments for quite some time.

***Keywords:*** *River, isotopes,oxygen-18, deuterium.*

## 1 Introduction

Stable isotopes (oxygen-18 and deuterium) are useful tracers for following water sources and evaporation processes. Specific sources and processes are known to cause certain isotope effects and their understanding enables one to use this tool. Isotope methods have found much application in groundwater and water ecological studies (Mook 2000). Surface water applications have been limited to work in the colder parts of the world and to evaporation studies.

An understanding of isotope processes occurring in the hydrological cycle is necessary to use this tool. Basically the rain input into a catchment will eventually emerge as runoff altered by mixing at various time scales (Talma and Vogel 2004) and evapo-transpiration processes. The stable isotope content of rainfall depends on the latitude, the mean annual temperature at the locality, the rainfall quantity and the distance inland from the sea (Mook 2000). Of particular importance at a fixed locality, is the amount effect which causes the $^{18}O$ and D content of high rainfall to be lower than that of the long-term average. The two isotope pairs (oxygen-18 and deuterium) behave in very similar ways. Globally the two isotopes are related by a simple relation called the Global Meteoric Water line (GMWL). At some localities there may be local meteoric water lines (Diamond and Harris 1997).

The loss of water by evaporation from an open body of water produces isotope fractionation. The process consists of a few steps, but the end result is an increase of the stable isotope composition of the water body remaining (Craig et al 1963). Oxygen-18 and deuterium behave differently during evaporation enrichment and this causes a distortion in the ratio between these two isotope pairs. A plot of deuterium against oxygen–18 is therefore a useful way to illustrate evaporation of water in nature (Simpson and Herzeg 1991). Transpiration by plants or directly from soils produces no isotope fractionation.

## 2 River sampling in 1968/73

In 1968 a network was established by the isotope laboratory at CSIR in collaboration with DWAF and others to collect weekly water samples from South African rivers. Isotope data, oxygen-18, deuterium ($^2$H) and tritium ($^3$H), of water from rivers draining 11 large and small catchments in southern Africa were collected and analysed on a weekly basis (Table 1). This was an attempt at that time to get an overview of the likely isotope variations in South African rivers. Sampling was discontinued in 1972-73.

The $^{18}$O time series for different rivers showed rapid (in the order of weeks) $^{18}$O decreases with increased runoff and gradual $^{18}$O increases with time during dry periods (summer or winter) (Talma 1987). The general pattern that was found in most rivers is one of a saw-tooth reflecting low $^{18}$0 during the rainy season and gradual enrichment of the water during base flow conditions (Figures 1-3). In general there was good negative correlation ($0.7 < R^2 < 0.85$) between the flow rate (on a log scale) of weekly samples and their $^{18}$O (Table 1): Exceptions to this pattern were found in those rivers (Zambezi, Vaal, lower Orange and Great Fish) for which the flow was, even at that time already, regulated by reservoirs. To quantify this effect, a reservoir index was defined as the ratio of the total storage capacity in the river upstream of the sampling point divided by the mean annual runoff at that point. Figure 4 shows that stations with high reservoir indices (i.e. more storage upstream) have lower correlation between $^{18}$O and flow. A refinement of this parameter would have to consider the position of the impoundment relative to the sampling site (e.g. to correct the anomaly of the Zambezi at Tete). This correlation enabled some sort of predictability of the $^{18}$O content of river water to be made for unregulated rivers.

We found that the volume weighted mean $^{18}$O content in a catchment is close to that of the weighted mean rainfall in the catchment (Talma 1987) which is useful to know for water balances. On the $^{18}$O time series it can be seen that low values are due to the larger rain storms with low $^{18}$O contents discharging in the rivers. During drier periods (or entire seasons) the water evaporates (either in embankments, or within the river), causing $^{18}$O in runoff to increase. Irrigation return flow is usually evaporated and will cause $^{18}$O to increase as well. Together these features generate the saw-tooth pattern observed in unregulated rivers with $^{18}$O negatively correlated to flow (log scale). As the Orange Bethuli example (Figure 2) shows, impoundment of water in a dam of any sizable volume reduces the variability of $^{18}$O in the water downstream. A water reservoir is a large mixed basin and the isotope variations tend to be smoothed out. Since the release of water from a dam down-stream is related to other factors than immediate inflow, there then is less correlation between $^{18}$O and flow rate (Figure 4).

Table 1. Details of the isotope sampling stations used during 1968/73 and their catchments.

| River | Sampling station | Sampling periods | Catchment area (km$^2$) | MAR (Mm$^3$/a) | Reservoir Index | $R^2$ |
|---|---|---|---|---|---|---|
| Kornetspruit | Maghalleen | 1971-72 | 3 050 | 627 | 0 | 0.78 |
| Orange | Oranjedraai | 1971-72 | 24 870 | 3951 | 0 | 0.73 |
| Caledon | Jammerdrif | 1971-72 | 13 315 | 1109 | 0 | 0.78 |
| Orange | Bethuli | 1968-70 | 65 380 | 8141 | 0.004 | 0.82 |
| | Gariep Dam | 1971-72 | | | | |
| Vaal | Douglas | 1968-72 | 193 765 | 3031 | 1.33 | 0.21 |
| Orange | Upington | 1968-70 | 260 400 | 12392 | 0.59 | 0.70 |
| | Upington | 1970-72 | | | 1.18 | 0.69 |
| Olifants | Mica | 1968-72 | 47 100 | 2615 | 0.15 | 0.71 |
| Tukhela | Mandini | 1968-72 | 28 910 | 3804 | 0.035 | 0.78 |
| Great Fish | Cookhouse | 1968-71 | 18 490 | 282 | 0.7 | 0.47 |
| Breede | Swellendam | 1968-72 | 9 829 | 2065 | 0.073 | 0.78 |
| Zambezi | Tete | 1970-73 | 900 000 | 81 360 | 2 | 0.60 |

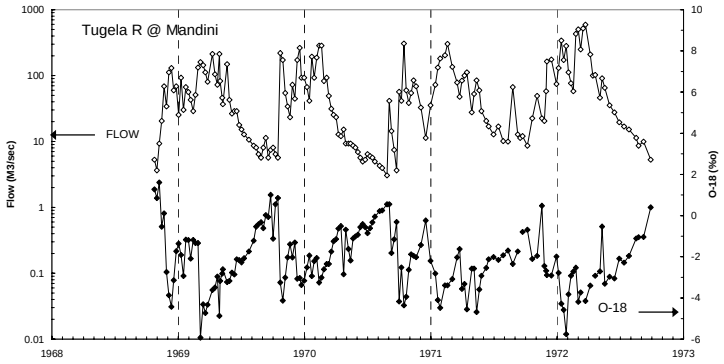


Figure 1. $^{18}O$ and flow (log scale) time series for the Tugela River at Mandini during 1968-73. Note the clear negative correlation between $^{18}O$ and flow.

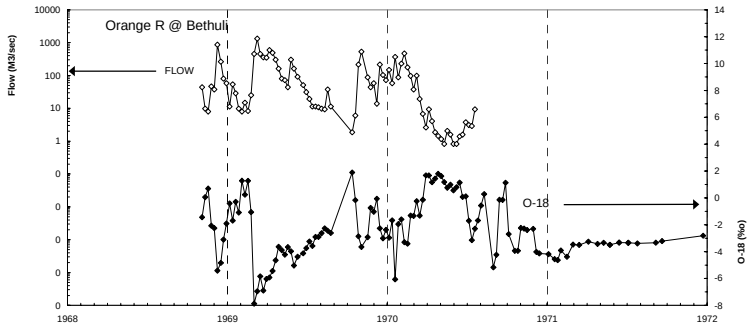


Figure 2. $^{18}O$ and flow (log scale) time series for the Orange River at Bethuli during 1968-71. The dam wall of the Gariep dam was completed in 1970 and started filling up in the summer of 1970/71. Note the stablisation of the $^{18}O$ variations in the water as the sample station became part of the well-mixed basin of the Gariep Dam.

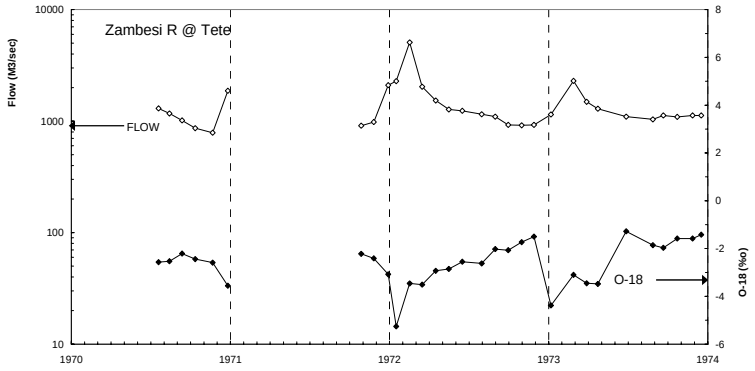


Figure 3. $^{18}O$ and flow (log scale) time series for the Zambezi River at Tete during 1970-73. The Kariba dam smoothes out any possible $^{18}O$ variation that may have entered the dam. There is still a summer dip noticeable at the sampling point further downstream.

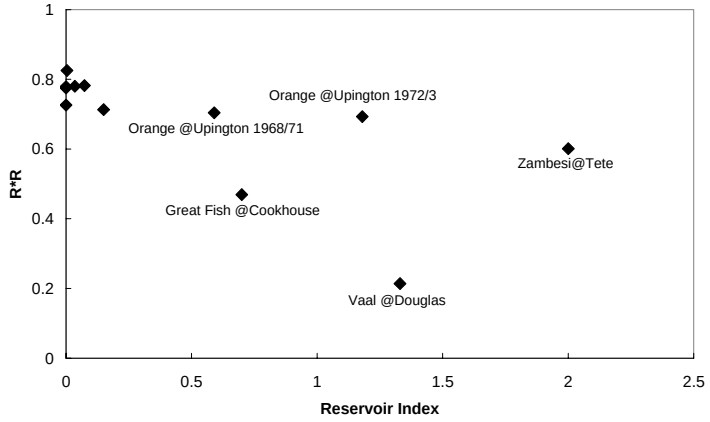


Figure 4. Plot of the regression coefficient between $^{18}O$ and log flow as function of the reservoir index calculated for the period 1968/73.

## 3 River sampling in 2002/5

Recently the application of isotopes in river water was given new life worldwide when a sampling program was initiated in 2002 as part of an IAEA (International Atomic Energy Agency) cooperative research project. The intention of IAEA (an agency of the UN to promote the peaceful use of nuclear technology) is to develop applications of isotope methods to study large river basins (IAEA 2002). Collaborators from a number of countries are also setting up similar networks. The newly constituted sampling network (Table 2) has been limited to the three larger rivers and includes the previously monitored sites in the Zambezi, Orange and Tugela rivers. There are now more sampling sites on each river since the details that can be revealed by down-stream differences are becoming more useful. Samples are collected monthly of fortnightly, but some interruptions were encountered at times. This new network now enables us to make comparisons of changes over 30 years. Deuterium data are being measured more extensively this time to indicate the extent of evaporation and different sources contributing to the total run-off at a site. This paper will concentrate on the $^{18}O$ effects observed.

Table 2. Details of the presently (2002/5) operating isotope sampling stations for the IAEA project.

| River | Location | Latitude south | Longitude east | DWAF Station reference | Catchment area km$^2$ | MAR Mm$^3$ /a |
|---|---|---|---|---|---|---|
| Orange | Oranjedraai | 30 20 10 | 27 21 34 | D1H009 | 24 870 | 4 000 |
| Orange | Gariep Dam | 30 37 23 | 25 30 26 | D3R002 | 70 749 | 8 000 |
| Orange | Van der Kloof Dam | 29 59 28 | 24 43 28 | D3H012 | 90 269 | 9 000 |
| Orange | Upington | 29 04 15 | 23 38 00 | D7H007 | 295 105 | 12 000 |
| Kl Boesmans | Estcourt | 29 00 08 | 29 52 54 | V7H012 | 196 | 30 |
| Tugela | Spioenkop Dam | 28 40 52 | 29 31 00 | V1H057 | 2452 | 1000? |
| Tugela | Mandini | 29 08 26 | 31 23 31 | V5H002 | 28 910 | 4 000 |
| Zambezi | Victoria Falls | 17 55 12 | 25 47 54 | | 507 200 | 33 500 |
| Zambezi | Kariba Dam | 16 30 58 | 28 47 00 | | | |
| Zambezi | Caia Ferry | 17 48 | 35 24 | only occasional sampling | | |

### 3.1 Orange River

In the Orange River (Figure 5) the 'classical' pattern is only partly visible at Oranjedraai (right on the South Africa/Lesotho border) in the sense that there is some saw-tooth pattern evident with minimum $^{18}O$ values at the end of summer. At present considerable quantities of water are already collected upstream in the Khatse and Mohale Dams and this has probably removed some of the variability that was evident in the earlier data set at Bethuli (Figure 2). At Gariep Dam further downstream, these variations are more smoothed out (Figure 5). From Gariep towards the van der Kloof dam there is gradual enrichment only in the 2004/5 season, probably due to evaporation along the way. At Upington the $^{18}O$ values are generally relatively high, which could be due to a contribution from the highly evaporated Vaal River, but is more likely due to the water use return flow and evaporation along the stretch between van der Kloof dam and Upington. River flow rates will be obtained to quantify these features.

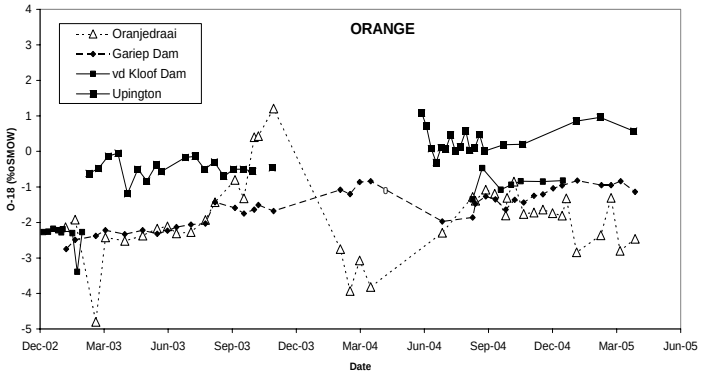


Figure 5. $^{18}O$ time series for the Orange River at four localities from Oranjedraai towards Upington during 2002-05.

### 3.2 Tugela River

In the Tugela catchment samples have been taken in two headwater quaternary catchments, at Spioenkop dam and in the Klein Boesmans near Estcourt, as well as at the mouth of the Tugela at Mandini (Figure 7). Significant depletion of $^{18}O$ during base flow is seen in the Klein Boesmans River but not in the Spioenkop Dam. The latter is clearly dampened by the reservoirs of the Tugela-Vaal scheme (Figure 6) while the Klein Boesmans River reacts with the classical swa-tooth pattern. However, $^{18}O$ enrichment is observed during low flows at the basin scale at Mandini. Comparison of the Tugela at Mandini data with those from 1968/72 at exactly the same site (Figure 1), indicates that present day $^{18}O$ values in the runoff could be higher by about 1‰ on an annual basis. The exact significance of this difference will become clearer when another season's data become available and flow data can be included in the comparison.

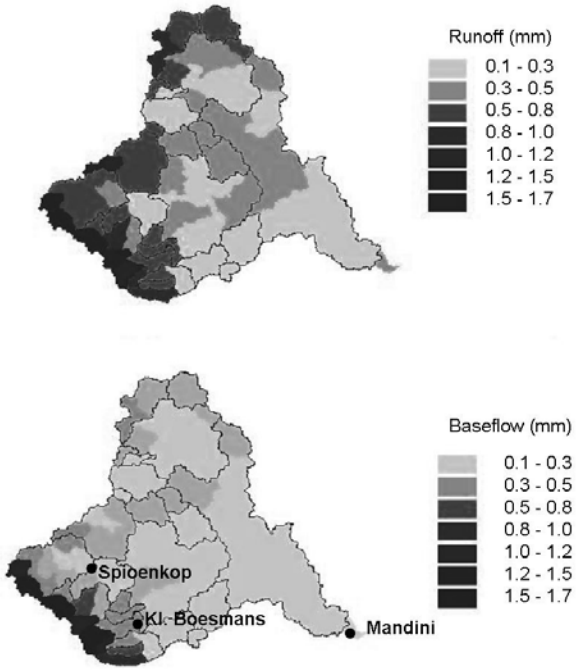


Figure 6. Modeling result of baseflow and runoff in the Tugela catchment

A deterministic hydrological model, ACRU, was used to simulate the runoff and the base flow in the catchment (Schulze 1996). This reveals that higher discharges of both runoff and baseflow are generated in the headwaters relative to the midlands and the coastal zone (Figure 5). Despite this, $^{18}O$ enrichment in the headwater samples from the Klein Boesmans is similar to the enrichment over the entire basin observed at Mandini (Figure 6). This suggests evaporative enrichment, not

only from the river and embankment, but also from the soil surface during the infiltration, lateral drainage and recharge processes, contributing to low flow generation. Shallow and deep groundwater isotope sampling has been proposed to confirm this.

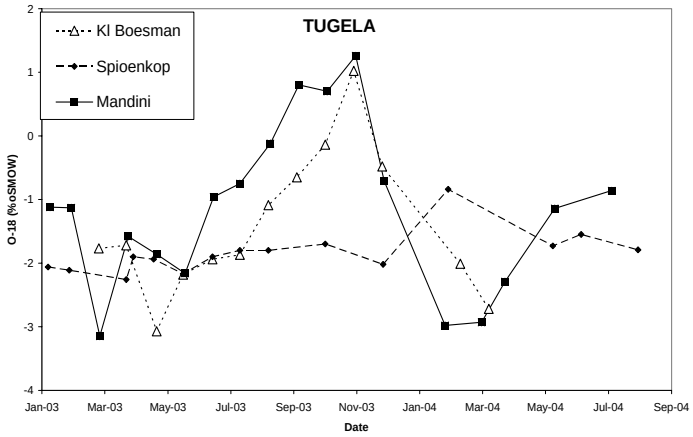


Figure 7. $^{18}O$ time series for the Tugela River at three localities during 2002-05.

### 3.3 Zambezi River

For the Zambezi River we were able to routinely sample two sites on the Zimbabwe side of the river. For the Mozambique part only opportunistic samples were delivered by occasional travelers across the Caia Ferry, close to the sea (Table 2).

The $^{18}O$ time series for Victoria Falls shows distinct dips in midsummer that corresponds to the high flow period (Figure 8). It was reported that the Zambezi flow at this site in February 2005 was the highest in six decades, yet the $^{18}O$ content that year was not lower than the preceding year. Lake Kariba has a capacity of many times its annual inflow. This explains the virtual lack of $^{18}O$ variation in its outflow: it is just one large evaporation pan. Further downstream additional sources of water (Kafue and Lake Malawi) enter the river and large amounts may accumulate in the Cahora Bassa Dam. These downflow components are probably responsible for the only $^{18}O$ dip in the present series, that in February 2003. This station is close to that of Tete sampled in 1970-73 during the construction of the Cahora Bassa Dam (Figure 3) and shows the same pattern of only a dip in midsummer. The base flow $^{18}O$ values at that time were in the range of –3 to -1‰ while at present it is between –2 and -1‰.

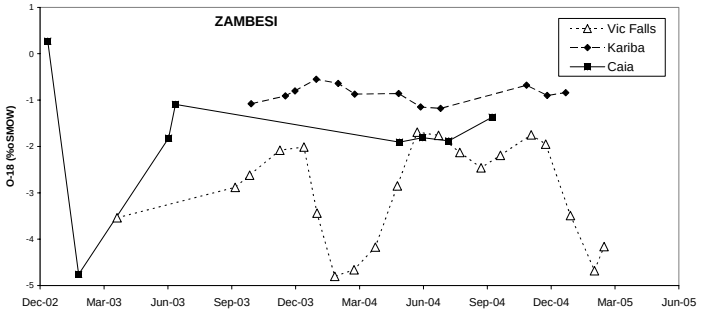


Figure 8. $^{18}O$ time series for the Zambezi River at three localities during 2002-05.

## 4 Conclusions

The early $^{18}O$ time series of a large number of rivers, most of them relatively undisturbed at that time, showed fairly simple and predictable saw-tooth patterns. The lower values are caused by high rainfall events with low $^{18}O$ contents due to the amount effect. After the main pulse of water has dissipated the water shows effects of evaporation. It is likely that this is evaporation of water in the interflow zone directly from the river bed or else there could be a component of return flow from water users along the river. Deuterium and chloride being analysed on the same samples, may become helpful here.

Impoundment of river water in large reservoir has the effect of smoothing out the isotope variations. The water from these dams then has the $^{18}O$ content of the weighted mean of the input and responds very slowly to variations of fresh input. This was quite clear to see in the Orange at Bethuli (Figure 2) when we happened to be sampling just during the time when the dam wall (of the then Verwoerd Dam) was completed and started to fill up. The Zambezi at Kariba and Tete also shows this stability of the isotope signal very clearly (Figures 3 and 8). In shallow dams there will be $^{18}O$ increases due to evaporation enrichment: removal of low $^{18}O$ water vapour causes the remaining water to increase its $^{18}O$ and deuterium content. It is possible that this is the feature seen in the Gariep and van der Kloof dam outflows (Figure 4) although it remains to be seen whether this enrichment quantitatively conforms to the predictions of the isotope enrichment model (Craig et al 1963).

The relation between $^{18}O$ and flow in undisturbed river is fairly predictable with $R^2$ values between 0.7 and 0.85 (see Table 1). In the case of rivers where dams and their management determine the water flow pattern, this correlation is weakened to such an extent that Zambezi $^{18}O$ and flow are constant except for a small blip at the end of the rainy season (Figures 3 and 8).

Collection of river samples from large catchments and analysis of the isotopes reveals that impoundments are effective in mixing flows and reducing variations in $^{18}O$ concentrations between high and low flows. However, where these variations can still be observed, they indicate significant evaporative enrichment during low flows. This enrichment is equally evident in headwater quaternary catchments as it is in flows derived from large basins. These observations suggest that enrichment occurs not only from evaporation from the river water body and embankment, but also from evaporation from soil profiles during replenishment of low flow generation sources such as water accumulated in hillslopes as well as groundwater aquifers. Sampling of these sources together with the river sampling will be valuable in defining the relative contribution of these sources to low flows and has been proposed for future investigation.

From a process point of view, the nature of the isotope increases during the dry seasons are of the greatest interest since these must be related to the nature of the interaction of base flow and groundwater. Tritium analyses of the Tugela samples between 1969 and 1971 have shown that a substantial part of the runoff at Mandini is older than 10 years (Talma and Vogel 2004). This means that there is a substantial amount of water that is delayed in the catchment and contributes to the base flow. These matters can be investigated by more detailed sampling using the right type of tracers and models.

## Acknowledgements

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